

AN EFFLORESCENCE ON SOME NEW ZEALAND  
KELPS.

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In December, 1910, I received a parcel of Algæ from Wellington, N.Z. After washing with fresh water and drying in the open air, I deposited specimens of some of the larger kelps, *Lessonia variegata* J. Ag., *Marginaria Boryana* (Rich.) Mont., and *M. Urvilleana* Rich., in a large cardboard box, and thus preserved them in a dry room. On looking over these specimens in June, 1915, I found them covered with a beautiful efflorescence of delicate needle-shaped crystals, some of them nearly a centimetre in length. They were singly colourless and flexible. The crystals had formed in such quantities that, by shaking the algæ, I was able to collect several grams of them. They were entirely soluble in water.

I made a large number of preliminary tests with them in the laboratory of the Sydney Grammar School. The flame was as pure a potassium flame as I could obtain from crystals of potassium chloride taken from the laboratory stock. I could not obtain any evidence of the presence of any other metal. The abundant precipitate with silver nitrate indicated that the potassium was mainly present as chloride. I could find no trace of sulphates or any other inorganic salts. There were no signs at all of iodine or bromine. That organic substances were present was soon discovered; and, notably, the reduction of copper sulphate in the presence of sugars showed the presence of OH radicals. The solution behaved just as would a solution of a tartrate or a citrate, while Fehling's solution gave no evidence of sugars. I could not obtain, however, independent evidence of the presence of tartrates or citrates.

I then made an exact determination of the amount of KCl. The samples selected were free from sand. In one sample, the percentage of KCl was 60.55, and in a second it was 61.24.

Speaking of the analysis to my friend, Mr. T. Steel, who has great laboratory experience in organic analyses, he evinced great interest in the matter, and offered to make a complete and exhaustive analysis of the efflorescence.

Mr. Steel's analysis gave:-

KCl ...	...	...	...	58.20
CaSO <sub>4</sub> ...	...	...	...	trace
Mannitol ...	...	...	...	36.70
Sand ...	...	...	...	4.90
Water ...	...	...	...	0.30
				100.10

He estimated the potassium and the chlorine separately, and thus definitely proved the complete absence of sodium.

If we deduct the sand, the percentage of KCl in the efflorescence is 61.3 and that of the mannitol 38.6. These percentages agree well with the formula of an exact chemical compound, C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub>, 4 KCl, as was pointed out by my colleague, Mr. Carpenter.

I then tried if this compound could be formed artificially in the laboratory. The chloride and mannitol were dissolved in the above proportions in a small quantity of water and evaporated down (1) rather quickly, and (2) very slowly in a desiccator. In the former case, the two substances crystallised out separately in their characteristically different crystalline forms. In the second case, crystals of one form only were obtained, needles arranged in beautiful feathery groups, crystals apparently identical with the crystals of the efflorescence.

I tried mixtures of alkaline chlorides with mannitol corresponding to the formula C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub>, 2KCl; C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub>, 4NaCl; C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub>, 2NaCl. In all cases, the substances crystallised out independently. No compound was formed.

The compound C<sub>6</sub>H<sub>8</sub>(OH)<sub>6</sub>, 4KCl is unstable in the presence of water, which dissolves more of the mannitol, and of alcohol,

which dissolves more of the chloride. On boiling with absolute alcohol, all the mannitol is precipitated.

Similar compounds of the alkaline chlorides with some of the sugars are already known.

It is, of course, well known that many of the kelps, or larger *Fucoideæ*, contain abundance of KCl in their ash. Efflorescence of salts on the dry weed is a common phenomenon in hot, dry climates. Whilst most published accounts of such efflorescences mention large quantities of KCl, they do not in general give anything else except NaCl. On the other hand, so long ago as July 31, 1894, in the Journ. Soc. Chem. Industry, Vol.34, p.608, C. Stanford writes, "Mannite is often seen on the frond of the *Laminaria* as an efflorescence, and is probably the result of fermentation." He does not mention the KCl.

A great deal of attention has been paid in the last few years to the constituents of kelps by American workers, and it is of interest to compare the results in the case of American kelps with those obtained from the New Zealand forms mentioned.

Mr. Frank K. Cameron, in Report No.100, United States Department of Agriculture, Washington, 1915, writes, p.21, "The salts contained in kelp are mainly potassium and sodium chlorides. To a small extent, calcium and magnesium salts and iodides are present, and probably unimportant amounts of other salts. While the ratio of potassium chloride to sodium chloride varies more or less, for general argument it may be assumed as approximately 3 to 2." And on p.27, "When kelp is dried slowly, there appears on the surface an efflorescence which can more or less readily be shaken off. This efflorescence is a mixture of potassium and sodium chlorides, the former predominating, together with smaller and generally negligible quantities of other salts." It will be noticed that there is no mention of a preliminary washing in fresh water, and the question arises— Is the sodium chloride actually derived from the kelp itself, or is it simply due to the evaporation of the adherent sea-water? No mention is made of the presence of mannitol in the efflorescence.

Mr. D. R. Hongland, writing in the Journal of Agricultural Research, U.S.A., Vol. iv., p.52, April, 1915, says, "The selective

action for potash is of course almost equally striking" [as that for iodine] "but the difference is of interest: much of the potassium chloride effloresces out as the plant dries, while no iodine is demonstrated in the effloresced salt."

In view of the above, Mr. Steel's complete analysis of an efflorescence undoubtedly derived solely from the algæ themselves, is of great value.

Mr. Hongland does not speak of mannitol, or of any other organic substance in the efflorescence, but, *l.c.*, p.47, speaking of the non-nitrogenous organic substances present in the kelp, he says, 'Very little information is obtainable for these groups, and there are no satisfactory chemical methods available for their study. In general, complex mucilaginous polysaccharines are characteristic of marine algæ, replacing the starch, cellulose, and simple sugars of most land-plants.' I do not know whether mannitol has been found in the dried weed. Stanford regarded it as an after-product produced by fermentation.<sup>o</sup> In the case of the New Zealand plants, the efflorescence is still forming (May, 1916), quite a large fresh crop of crystals having appeared in the interval from June, 19'5. It seems improbable that a fermentation could continue for five years and a half under dry conditions. I imagine that the efflorescence is a purely physico-chemical phenomenon.

It would be premature to discuss the bearing of the result of the analysis of this efflorescence upon the subject of the metabolism of kelps.